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Seasonal and inter-annual variations of nitrogen diagenesis in the sediments of a recently impounded basin

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Abstract. The Méry-sur-Oise (France) storage reservoir is an artificial basin of 9 m average depth, fed by water from the river Oise with a mean residence time of about 4 days. Sediments are accumulating at a rate of about 0.7 cm/month. In the sediments, two fractions of organic nitrogen with different rates of bacterial degradation could be distinguished, one associated with fresh phytoplankton, the other made of detrital and more refractory compounds. The fluxes of oxygen, nitrate and ammonium across the sediment-water interface were measured with a bell-jar system at different seasons during a 3 year period following flooding of the basin. The measurements show clear seasonal variations in relation with the variations of temperature and input of fresh phytoplanktonic material to the sediment. In addition, a long term trend of increasing ammonium was observed. Measurements were also carried out after dredging of all accumulated sediments of the basin. They showed a considerable reduction of the flux of nitrate to the sediments and a significant reduction of the flux of ammonium to the water column.

These results are interpreted in the light of a non stationary model of N diagenesis in accumulating sediments. This model is able to predict at least the general trends of benthic N cycling of basins during the early stage of their ecological succession.

Introduction

The importance of benthic processes in nutrient dynamics of shallow aquatic ecosystems is now largely recognized (Rowe et al. 1975, 1977; Billen 1978; Fisher et al. 1982; Hopkinson & Wetzel 1982; Blackburn & Henriksen 1983, Billen & Lancelot 1988). Recently flooded basins, however, are systems initially deprived of a benthic phase and where a gradual accumulation of sediments occurs. The development of a progressively deeper sedimentary column can result in a slow change in the ecological function of the whole ecosystem. This paper reports observations of sediment deposition and nitrogen accumulation, transformation and recycling, in an artificial basin fed by river water, during three years following its filling. The basin is used as a storage reservoir for a drinking water plant. This work was carried out with the purpose of establishing a mathematical model of the basin allowing to predict the effect of storage on water quality and to define the best management of the basin and its sediments.

In the study of nutrient diagenesis in recent sediments, it is often assumed that steady-state conditions are established. This assumption greatly simplifies the interpretation of experimental data on vertical concentration profiles within the sediments. It allows derivation of simple mathematical models which, among other things, permit calculation of the fluxes across the water-sediment interface (see e.g., Berner 1980; Billen 1982). The steady-state assumption rigorously requires the time-independence of all conditions prevailing in the sediments, including sedimentation rate and composition of sedimented material. However, several studies have demonstrated that important seasonal variations occur in nutrient regeneration rates in response to the variations in temperature and the input of fresh phytoplanktonic material to the bottom (Davies 1975; Kaplan et al. 1979; Klump & Martens 1981; Graf et al. 1982; Blackburn & Henriksen 1983; Sorensen 1984; Wassmann 1984, 1986). Another implicit assumption implied by the steady-state hypothesis is that the sedimentary column can be considered as infinite, so that deposition of additional layers of sediment does not alter the conditions prevailing near the interface. This assumption is of course invalid in the case of recently impounded basins or ponds which develop entirely new sedimentary layers within a few years.

The observations reported in this paper offer a unique opportunity to study both seasonal and long term variations in nitrogen diagenesis in a recently flooded basin and to develop a simple model of these variations.

Biotope and methods

The basin of Méry-sur-Oise (50 km NE of Paris) is an artificial basin, fed by the river Oise and used as a storage reservoir for a drinking water plant managed by the Compagnie Génèrale des Eaux. Its volume is about 400 000 m^3, with an average depth of 9 m. It was dug within the alluvial gravels of the river, and insulated from it by watertight wall. It was flooded in July 1980. Water from the Oise is intermittently injected with pumps into the basin in such a way as to prevent stratification of the water column, without causing resuspension of the sediments. The mean residence time of the water in the basin is about 4 days.

Undisturbed sediment samples were taken with an Eckman box-corer.

Subsamples were immediately frozen and cut into 1 cm slices. Pore water was extracted by centrifugation. Nitrate and ammonium were determined following the methods of Amstrong et al. (1967) and Slawyc & Mc Isaac (1972), respectively. Organic carbon in the solid phase was determined with a LECO Carbon Analyser. Organic nitrogen determinations were performed with a standard micro Kjeldahl procedure. Adsorbed ammonium was extracted twice with 2M KCl. Chlorophyll and phaeopigments determinations were made following the method of Lorenzen (1967). For determining the exchanges across the sediment-water interface, a 10 l bell-jar with a slow stirring system was deposited on the bottom. Water samples from inside the bell were pumped each hour from the surface for nitrate and ammonium analysis. Oxygen concentration was continuously recorded by a YSI Oxygen-probe.

Results

Sedimentation rate

The rate of sediment deposition in the basin was determined by two methods.

On two occasions, during a partial emptying of the basin 9 and 33 months after the initial flooding, the depth of the sedimentary column overlying the gravel bottom was measured at about 30 stations. The results are summarized in Fig. 1. They show a mean thickness for the layer of accumulated sediments of 6.3 and 22 cm after 9 and 33 months, respectively. This indicates a constant mean sedimentation rate of approximatively 0.7 cm.month^{-1} over the two periods.

A budget of the input and output of suspended matter in the basin was also established for the years 1981 and 1982 based on bimonthly measurements of suspended matter concentration in the river Oise and in the basin, and on the daily discharges of water pumped through the basin. The details of these calculations are given in Table 1. A sedimentation rate of 0.84 and 0.68 cm.month^{-1} is calculated for 1981 and 1982 respectively. These figures are in good agreement with the value found on the basis of direct measurements of the thickness of the sedimentary layer.

From the end of August to the beginning of November 1984, the sediments were entirely dredged by aspiration. Direct observation by divers at 60 stations in November 1984 showed that the residual sedimentary layer was reduced to 5–10 cm.

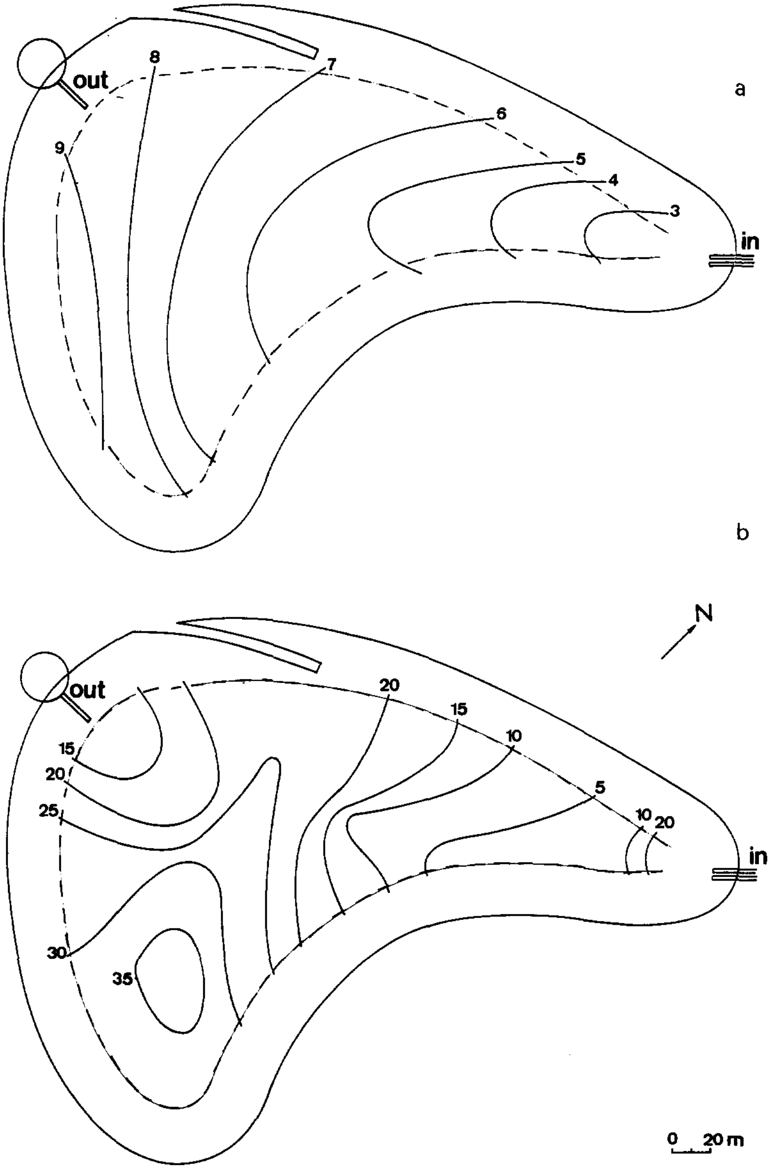


Fig. 1. Maps of the storage basin at Méry-sur-Oise showing the depth (in cm) of the sedimentary layer on (a) 7th May 1981 (9 months after flooding), (b) 20 April 1983 (33 months after flooding). in: River water injectors out: Offtake to the plant

Table 1. Budget of suspended matter in the basin of Méry-sur-Oise for 1981 and 1982.

Year		1981	1982
Annual discharge of river water	($10^6 m^3$. year^{-1})	35.8	47.5
Input of suspended matter (1)	(10^9 g. year^{-1})	2.8	2.63
Output of suspended matter (2)	(10^9 g. year^{-1})	0.71	0.93
Sedimentation	(10^9 g. year^{-1})	2.09	1.70
Sedimentation rate (3)	(cm. month^{-1})	0.84	0.68

(1) calculated as $\int Q \cdot X_0 dt$
1) where Q is the discharge of river water injected into the basin
X_0 is the concentration of suspended matter in the river water

(2) calculated as $\int Q \cdot X_0 dt$
where X_B is the concentration of suspended matter in the basin

(3) Calculated with the following data:

total basin area	: 45 000 m^2
sediment porosity	: 80%
density of dry sediments	: 2.3 g.cm^{-3}

Fluxes organic matter to the sediments

The organic matter content of the suspended matter in the basin varies a lot, being higher in spring and summer (up to 15% organic C) than in winter (around 4–9% organic C), owing to the higher concentrations of phytoplankton.

The ratio of particulate organic carbon to total chlorophyll *a* pigments (chlorophyll *a* + phaeopigments *a*) is plotted against chlorophyll *a* pigments in Fig. 2. As seen, this ratio decreases asymptotically to a constant value of 30 with increasing pigments concentrations. This value has been considered as characteristic of phytoplankton composition, and has been used for calculating the contribution of fresh phytoplanktonic material to total particulate organic carbon, from the measurements of pigments concentration. Thus Fig. 3 shows the seasonal variations of the content of suspended matter in fresh planktonic and detrital organic carbon, calculated from the data observed in the basin during the year 1982. It indicates that the concentration of detrital carbon in the suspended matter does not vary much around a mean value of 4.5%, while the concentration of phytoplanktonic material varies a lot, with maximum in spring and fall.

This leads us to consider separately two fluxes of organic material to the

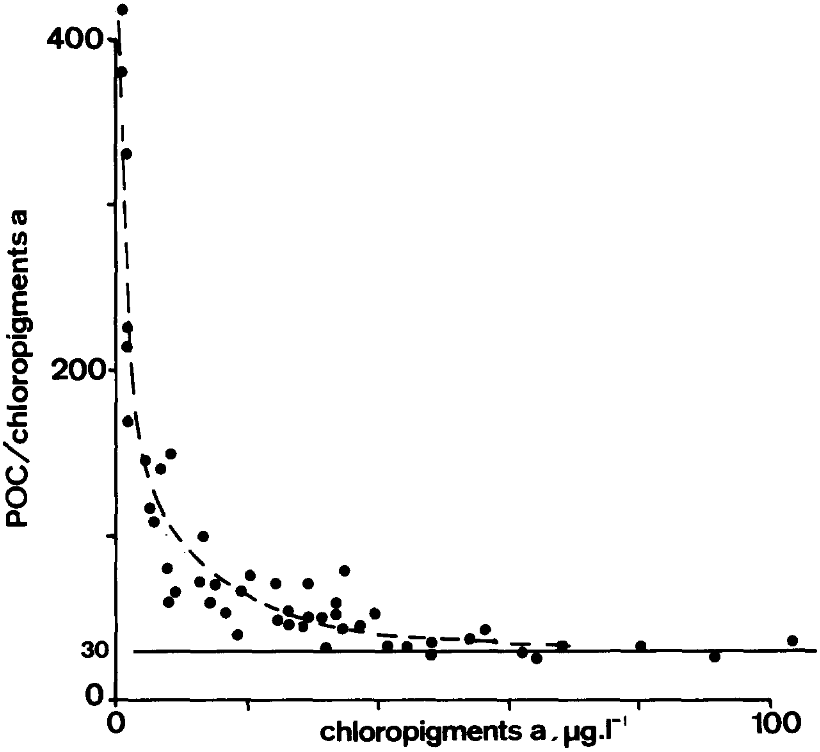


Fig. 2. Observed relationships between the ratio of particulate organic carbon (POC) to total chlorophyll pigments (Chlorophyll *a* + phaeopigments) and total chlorophyll *a* pigments in the storage basin of Méry-sur-Oise. The asymptotic value at high pigments concentrations is used for calculating phytoplanktonic carbon from pigments values.

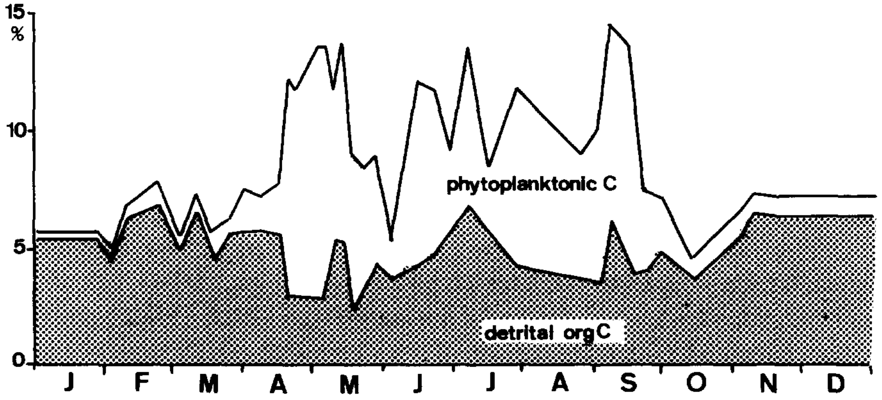


Fig. 3. Observed seasonal variations of phytoplanktonic and detrital organic carbon content of suspended matter in the Oise River in 1982.

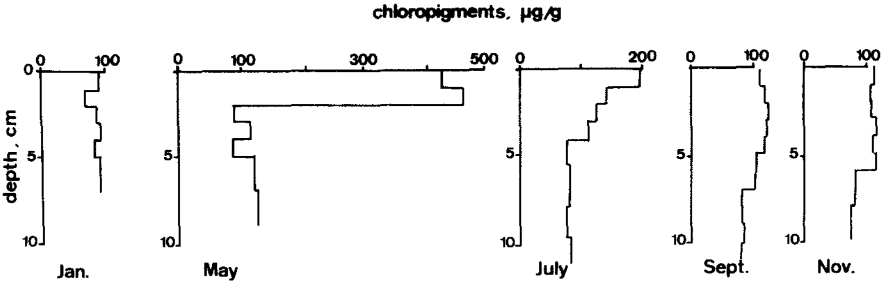


Fig. 4. Vertical profiles of chlorophyll *a* and associated phaeopigments in the sediments of the basin of Méry-sur-Oise from January to November 1982.

sediments: a reasonably constant flux of detrital organic matter, and a seasonally variable flux of fresh phytoplanktonic material.

Although no clear variations in the total organic carbon content of the sediments could be detected, important seasonal variations of the content of chlorophyll pigments in the top sediment layer were observed (Fig. 4). A conservative estimate of the flux of phytoplanktonic material to the bottom

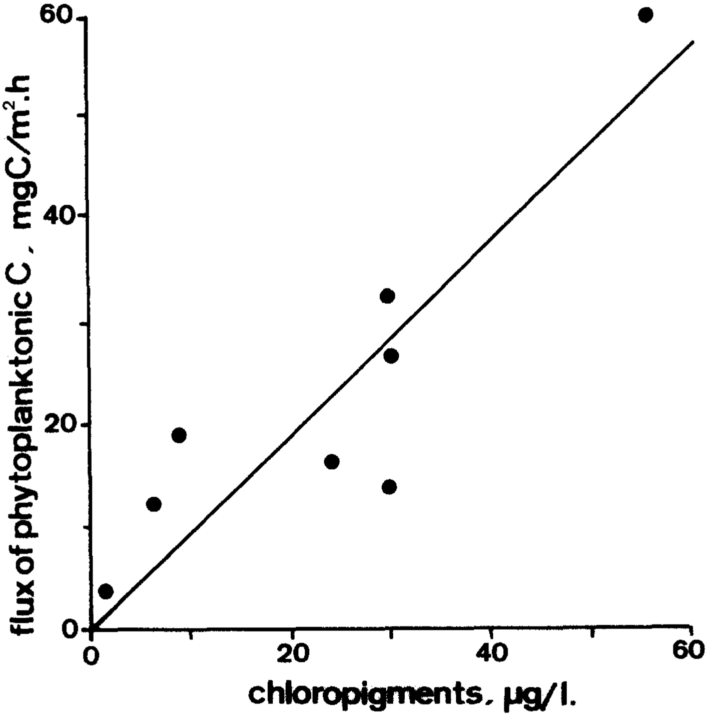


Fig. 5. Relationships observed between the flux of phytoplanktonic material deposited on the sediments and the concentration of phytoplankton in the water column.

can be obtained by multiplying the observed concentration of phytoplanktonic organic carbon in the top 0–1 cm by the sedimentation rate determined above. The obtained values correlate significantly with the value of chlorophyll concentration in the water column (Fig. 5) and allow calculation of a net sedimentation rate constant (k_F) for phytoplankton of about 0.032 m.h^{-1}. This value compares well with the range of sinking rates values reported by Bienfang & Harrison (1984) for various net phytoplankton species (0.01–0.07 m.h^{-1}).

Vertical distribution of C and N species in the sediments

Organic carbon concentration in the solid fraction of the sediments shows only a very slow decrease with depth (Fig. 6a). Below 10 cm, the mean organic carbon content is still 4.5%, a value very close to the mean value of detritic organic carbon concentration in suspended matter. Organic nitrogen content displays the same pattern of vertical distribution (Fig. 6b). The C/N ratio of the organic material is about 7 in the upper sediment layer and 8.5 at 10 cm depth.

Nitrate concentration in the interstitial water decreases rapidly from 250–300 μmol.l^{-1} at the water-sediment interface (concentration found in the water column) down to zero below 3 cm depth. Dissolved ammonium concentration in the pore water (Fig. 7) is only a few μmol.l^{-1} at the water-sediment interface. It increases rapidly with depth in the 5–7 upper sediment layer and then reaches a plateau. The concentration reached below 7 cm depth shows a clear long term increase, from about 500 μmol.l^{-1} in

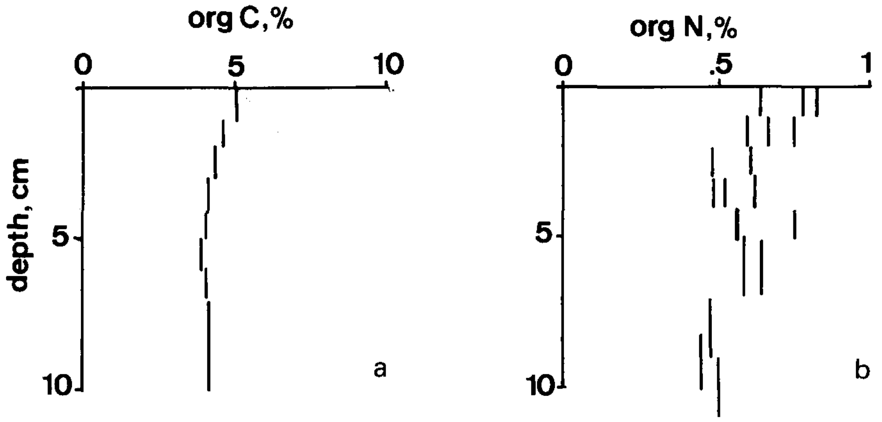


Fig. 6. Vertical profile of organic (a) and nitrogen (b) in the solid phase of the sediments. Composite data from August 1981, January and April 1982.

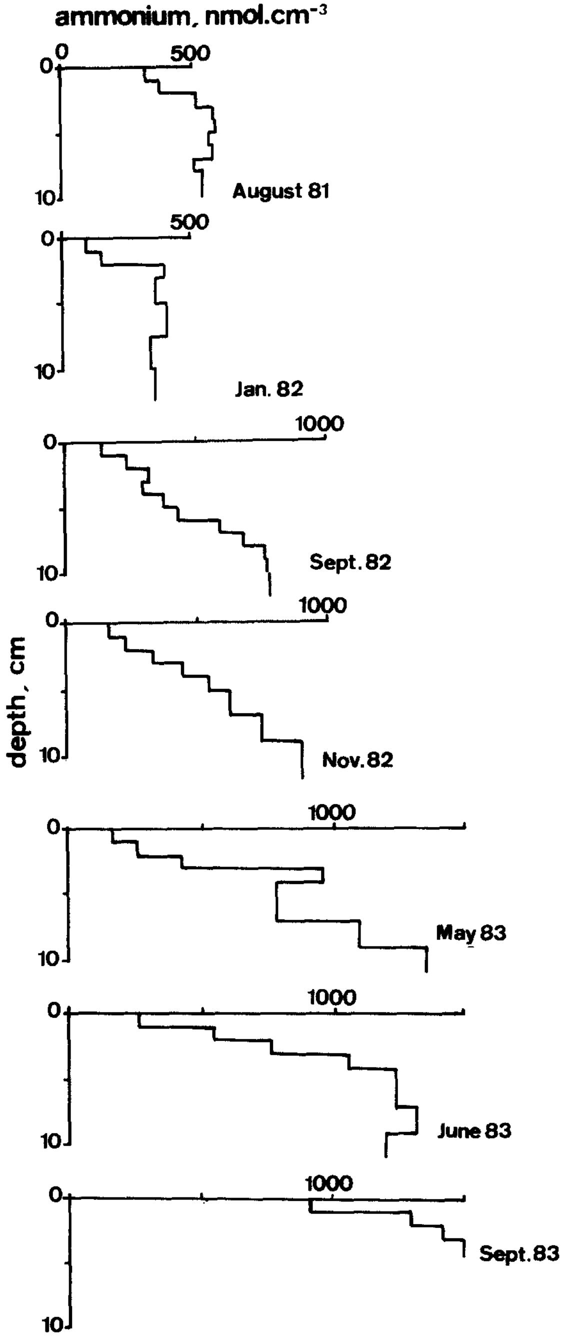


Fig. 7. Long term evolution of the vertical profiles of ammonium concentration in the interstitial water of the sediments, as observed from 1981 to 1983.

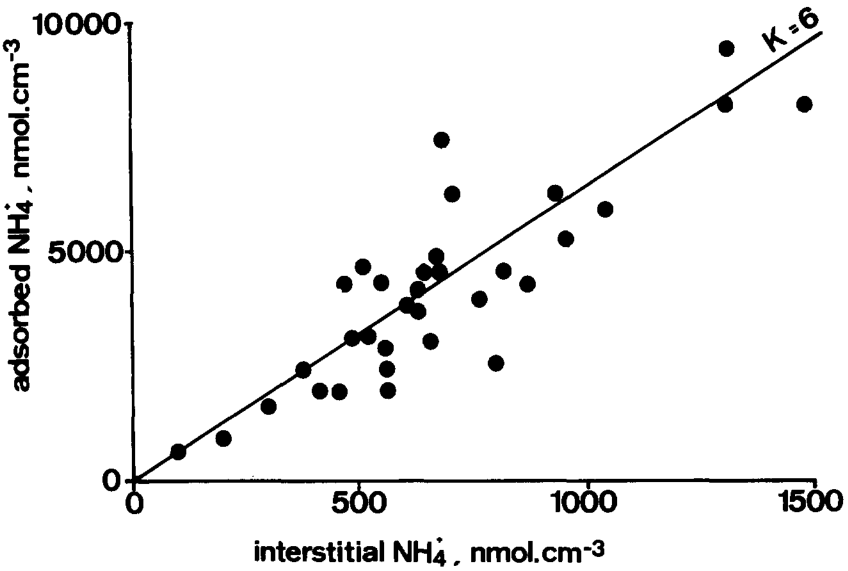


Fig. 8. Relationship between adsorbed and dissolved ammonium concentration in the sediments.

1981 to 1500 μmol.l^{-1} in 1983. The concentration of adsorbed ammonium on the solid phase of the sediment is proportional to the ammonium concentration in the interstitial water as shown in Fig. 8. The adsorption constant K, equal to the ratio of adsorbed to dissolved ammonium concentrations, both expressed per unit volume sediment, is about 6.

Rate of microbiological processes in the sediments

The strong decreasing gradient of nitrate concentration in interstitial water of the sediments indicates active denitrification. In order to determine the rate of this process, nitrate was added to a sample of sediments from the upper 3 cm layer and the concentration was followed during a 1 h incubation at 20 °C. The results display a very rapid disappearance of nitrate, according to a first order kinetics. The value of the kinetic constant at 20 °C range between 2.9 and 4.3 h^{-1}.

The rate of ammonification in the sediments was determined in samples taken at different depths from a core by following the increase of dissolved and adsorbed ammonium concentration during ten days incubation at 20 °C. The results are presented in Fig. 9. They show a rapid decrease with depth in the 3 upper cm, followed by a slower decrease below 4 cm.

It is likely that the high rates measured in the upper layers correspond to the degradation of fresh, phytoplanktonic material, while the lower, only

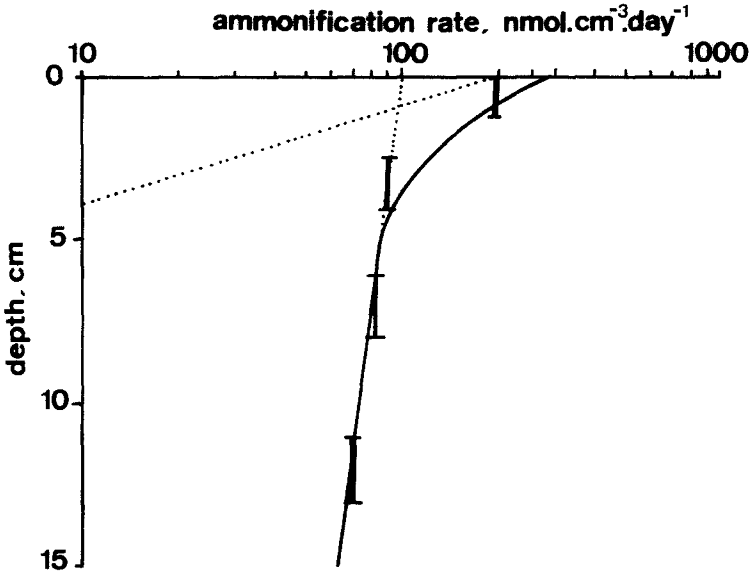


Fig. 9. Vertical distribution of the rate of ammonification in the sediments (incubation at 20 °C). The dotted lines represents the assumed respective contributions to total ammonification rate of the degradation of detrital and fresh phytoplanktonic material.

slowly decreasing rates measured in depth correspond to the degradation of detritic organic matter.

Exchange of dissolved substances across the sediment-water interface

The fluxes of oxygen, nitrate and ammonium across the sediment water interface were measured with the bell-jar system from spring 1982 to spring 1985. The data (Fig. 10) show clear seasonal variations, with maximum values in the spring and summer. In the case of ammonium, a definite long-term increasing trend of the flux is observed over the three year period.

The effect of dredging can be assessed by comparing the fluxes measured just after dredging in November 1984 with the values observed at the same season in previous years. The flux of ammonium is reduced to undetectable values. The flux of nitrate is reduced by a factor of 4–5. No significant reduction is observed for the flux of oxygen.

Discussion

Budget of nitrogen transformations in the sediments

With the data presented above, it is possible to establish a budget of nitrogen transformations in the sediments. This has been done, as an example, for

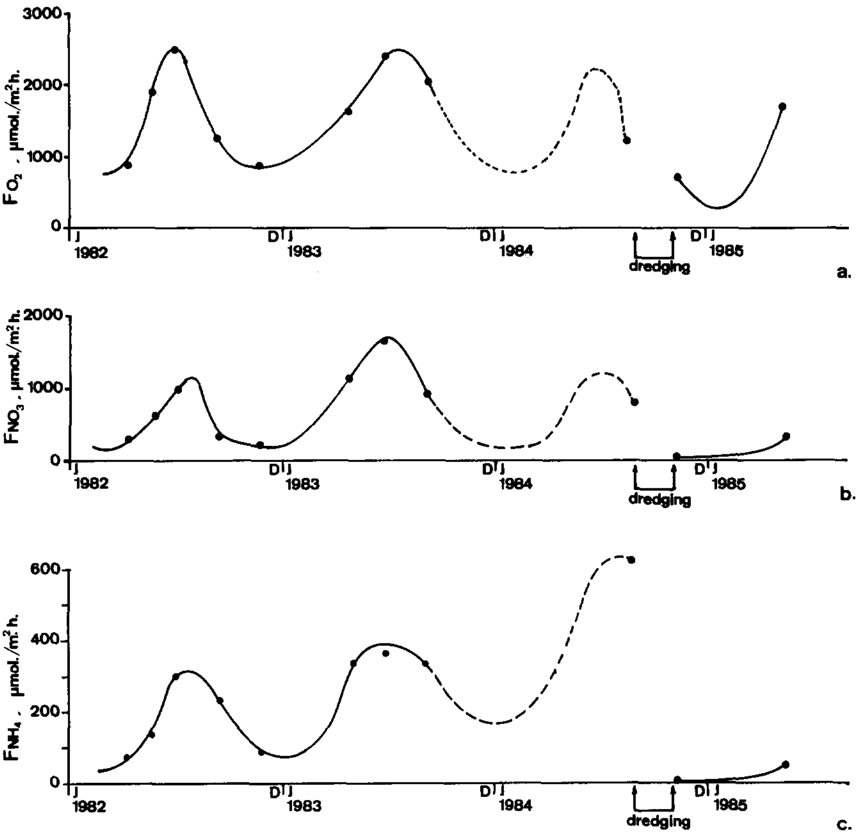


Fig. 10. Seasonal and long term evolution of the measured flux of oxygen (a), nitrate (b) and ammonium (c) across the sediment-water interface, between 1982 and 1985. The arrows indicate the time of dredging. Note that oxygen and nitrate fluxes are directed to the sediment while ammonium is released to the water column.

two periods:

— in early April 1982, 20 months after flooding of the basin, in a period without important phytoplanktonic development;

— in mid-June 1983, i.e., 44 months after flooding, in a period of phytoplanktonic bloom.

For the two situations, the flux of detritic particulate organic nitrogen to the sediments was calculated on the basis of the mean sedimentation rate on the one hand and the mean nitrogen content of the suspended matter in the absence of phytoplankton (0.65%) on the other hand. The flux of phytoplanktonic nitrogen was calculated from chlorophyll concentration in the basin and the sedimentation constant determined above.

As suggested by the data of Fig. 9, the ammonification rate is considered as made of two parts. One corresponding to the degradation of detritic organic material, which is calculated by extrapolating the rates of ammonification found below 3 cm to the whole sedimentary column, and the other corresponding to the degradation of fresh phytoplanktonic material, which is calculated as equal to the flux of this material to the sediments, considering a C/N ratio of 5.6 (Redfield et al. 1963).

The rate of accumulation of the various nitrogen species is calculated from their concentrations in the sediments and the value of the sedimentation rate. The fluxes of ammonium and nitrate across the sediment-water interface were experimentally determined. The rates of nitrification and denitrification are evaluated by difference. The results of these calculations are shown diagrammatically in Fig. 11.

In the two situations considered, the sediment acts as a very efficient sink for nitrogen: the output of nitrogen to the water column is respectively 3.2 and 5.4% of the total inputs to the sediments. This is mainly the result of two processes:

- burial of detrital organic nitrogen, which is only slowly decomposed by microbiological activity;
- denitrification, which reduces not only the nitrates produced by nitrification in the aerobic layer of the sediment, but nitrate from the water column as well.

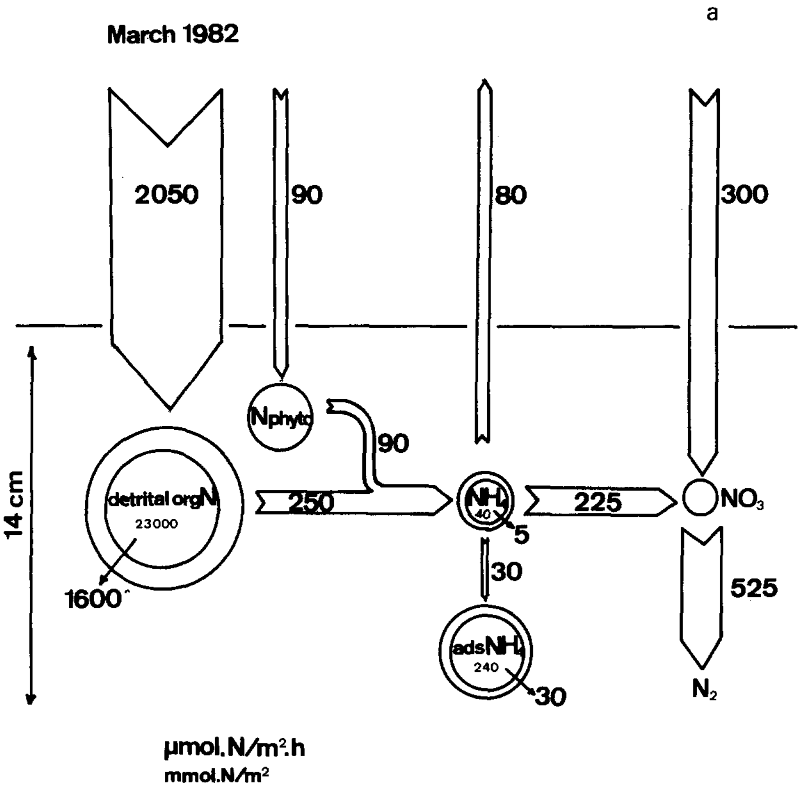
The differences observed in Fig. 11, between the two situations, result partly from the deeper sedimentary column build up in June 1983 (24 cm) with respect to March 1982 (14 cm), and partly from seasonal differences in temperature and in the flux of fresh phytoplanktonic material. The following model will try to take these two effects into account for predicting the short-term and long-term variations of nitrogen diagenesis during the first years after flooding of the basin.

Model of nitrogen diagenesis in the sediment

The model was developed according to general principles of the diagenetic analysis (Berner 1980), allowing to relate the fluxes of chemical species across the sediment water interface to the vertical distribution of the rate of the processes affecting them. The basic assumptions of the model are the following. The detailed calculations are explained in the appendix.

Organic matter deposited on the sediments is made of two fractions of different origin and properties:

- a rapidly degraded fraction $Corg_1$, of phytoplanktonic origin, with a C/N ratio of 6 and a first order degradation constant ka_1. The flux of this material to the sediments ($Forg_1$) varies seasonally, following algal



blooms in the water column;

— a slowly degraded fraction, $Corg_2$, of detrital origin, with a C/N ratio of 8 and a first order degradation constant ka_2. The flux of this material to the sediments is considered as constant.

The sedimentary column increases at a constant rate ω. Mixing of the solid phase of the sediments by bioturbation is neglected; the dispersion of dissolved substances in the interstitial water is characterized by an apparent mixing coefficient Di of $5\ 10^{-5}\ cm^2/sec$ (Billen 1982) estimated by comparing the measured value of nitrate flux with the estimated concentration gradient at the sediment water-interface.

It is assumed that a stationary state is reached instantaneously for the rapidly degraded fraction $Corg_1$, as well as for all dissolved species, while the profile of the slowly degraded organic fraction $Corg_2$ is assumed to be near equilibrium with respect to the annual mean conditions. With these simplifying but reasonable assumptions, the only non stationarity to be taken into account in the mathematical solution of the diagenetic equations lies in the gradual increase of the depth of the sedimentary column.

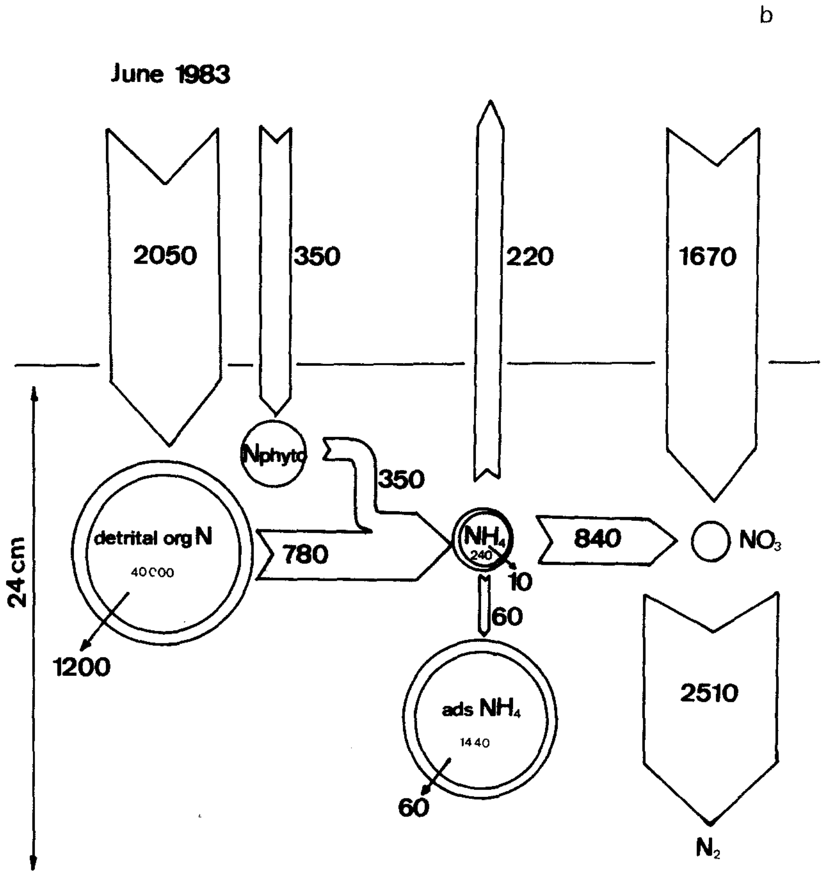


Fig. 11. Flow diagram of the nitrogen transformations within the sediments and exchange with the water column in (a) March 1982 (prebloom period, 20 months after flooding of the basin) and (b) June 1983 (bloom period, 35 months after flooding of the basin). Reservoirs in mmolN/m^2, fluxes in μmolN/m$^2\cdot$h.

The approach consists in first calculating the depth distribution of the two fractions of organic matter, knowing:

— the time elapsed from the flooding of the basin which determines the depth of the sedimentary column (ωt);

— the mean annual deposition rate of refractory organic matter, which is considered to remain constant at the value of 0.20 gC/m^{-2}.h^{-1}, corresponding to the mean deposition rate of 0.7 cm/month and the mean value of detrital organic carbon content in suspended matter of 4.5%;

— the instantaneous deposition rate of fresh phytoplanktonic material which varies seasonally. It is calculated from the mean observed annual variations of chlorophyll *a* in the water column (Fig. 12a) and the value

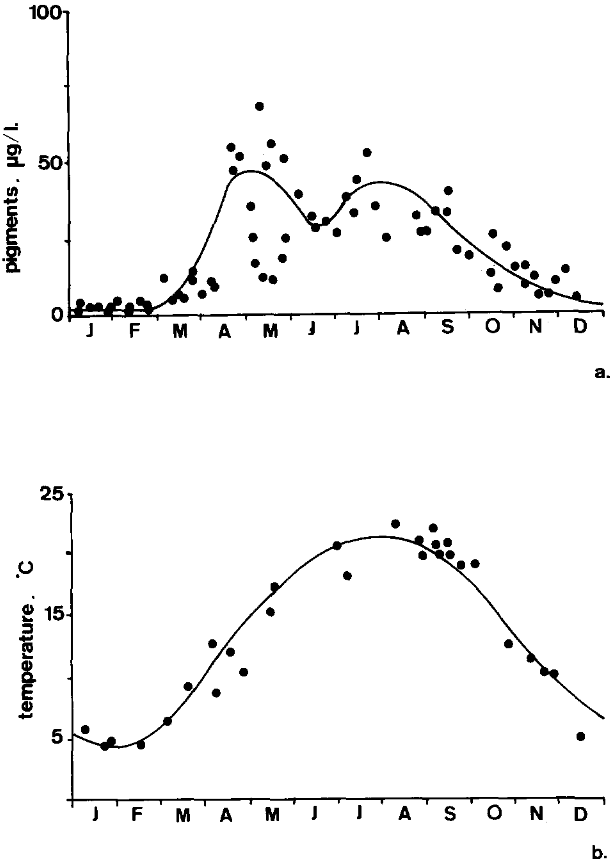


Fig. 12. Observed seasonal variations of chlorophyll *a* concentration (a) and temperature (b) in the water column of the basin of Méry-sur-Oise. (Dots refer to observations made in 1981, 1982, 1983. Solid curve is the smoothed mean of these observations used in the model).

of 0.032 m.h^{-1} determined above for the sinking rate of phytoplanktonic material.

From this, the vertical distribution of the rate of organic matter degradation and hence, ammonification can be calculated. By adjustment of this theoretical distribution to the experimental data of Fig. 9, the values of ka_1 and $\overline{ka_2}$ (annual mean value) can be evaluated to 3.6 10^{-4} (at 20 °C) and 2.1 10^{-5} h^{-1}, respectively. The effect of the observed variations of temperature (Fig. 12b) on the parameter ka_1 is taken into account by considering a Q_{10} of 2.

From the knowledge of the vertical distribution of the rate of organic matter degradation, the flux of benthic oxygen consumption and the oxygen penetration depth (z_n) can be calculated. This is important because it also determines the depth of the layer where nitrification occurs. It is assumed

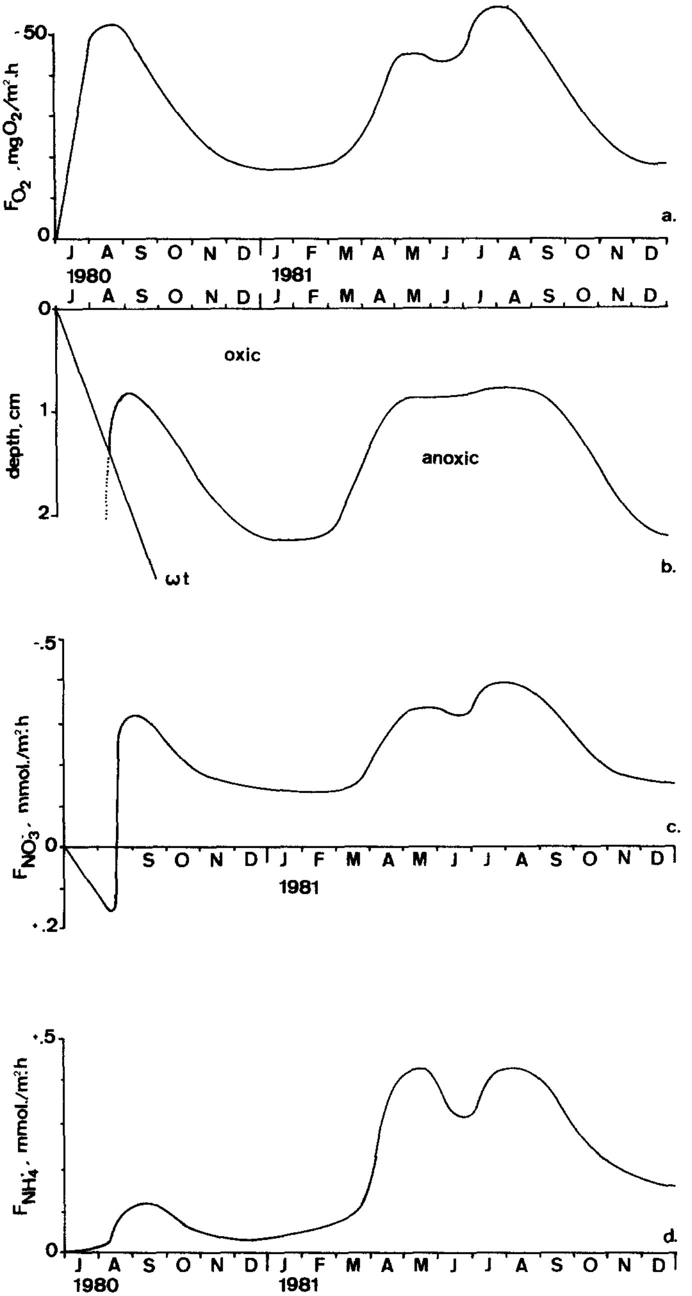


Fig. 13. Simulation with the model described in the text of (a) oxygen flux across the sediment-water interface; (b) depth of the oxic layer of the sediment; (c) nitrate flux across the sediment-water interface; (d) ammonium flux across the sediment-water interface, during 1.5 year following flooding of the basin.

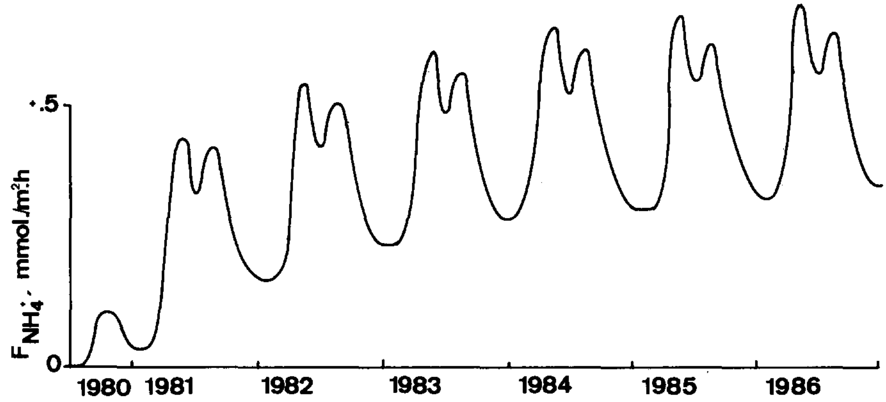


Fig. 14. Simulation of the long term variations of the ammonium flux to the water column, according to the model described in the text.

that, in the oxygenated layer, 80% of the flux of ammonification is nitrified (Billen 1982). Below this oxygenated layer, denitrification occurs at a rate determined by the availability of both nitrate and organic matter. The balance between nitrification and denitrification determines the flux of nitrate across the sediment-water interface.

For calculating the concentration profile and the flux of ammonium, the process of adsorption is taken into account, as well as ammonification and nitrification.

Figures 13a, b, c and d present the results of these calculations for a two year period following flooding. Figure 13a presents the calculated flux of oxygen across the water-sediment interface. During the first 40 days after flooding, the sedimentary column is shallow enough for being entirely oxic ($z_n > \omega t$) (Fig. 13b), and the oxygen flux to the sediment increases with the depth of the accumulated sediments. Later on, an anoxic layer develops and the oxygen flux undergoes only recurrent seasonal changes in response to the variations of temperature and input of fresh phytoplanktonic material (Fig. 13a).

During the period of time when the whole sedimentary column is oxic, no denitrification occurs and the flux of nitrate is directed to the water column as a result of nitrification (Fig. 13c). As soon as the anoxic layer develops, denitrification rapidly dominates, reducing not only all nitrate produced by nitrification in the oxic layer but an important amount of nitrate from the water column aswell. At the end of the first period after flooding, this results in an inversion of the nitrate flux across the sediment-water interface.

The flux of ammonium is rather low during this first period, because most ammonium produced is oxidized by nitrification (Fig. 13b). It increases

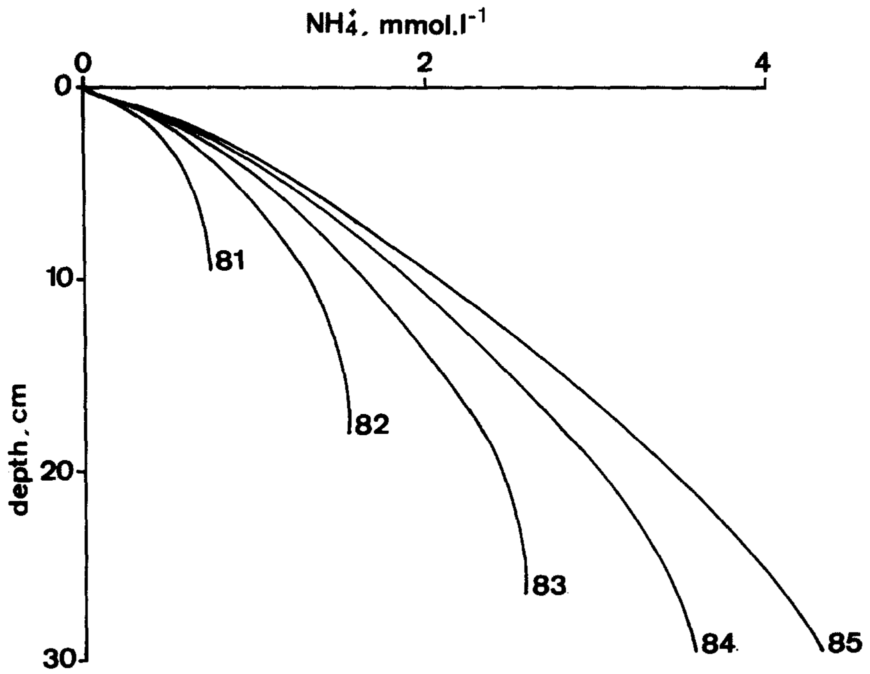


Fig. 15. Simulation of the long term variations of the vertical profiles of ammonium in the interstitial water of the sediments, during 5 years following flooding of the basin.

considerably when the anoxic layer develops. For more than 5 years after flooding, it undergoes seasonal variations super-imposed to a long term increasing trend (Fig. 14). This long term increase is due to the increasing contribution to the total ammonification rate of the slow degradation of detrital organic matter accumulated in the thickening sedimentary column. The calculated vertical profiles of ammonium concentration in the interstitial water show the same trend of long term increase (Fig. 15), in good agreement with the observations (Fig. 7) performed from August 1981 to September 1983.

Conclusions

Recently impounded or dredged basins are rapidly evolving ecological systems. The gradual development of a sedimentary column is one of the major aspects of their evolution. The observations and calculations described in this paper offer an interesting account of the change occurring in the nitrogen cycle of an artificial reservoir during a few years after flooding, as a result of the progressive accumulation of sediments.

Because of the burial of slowly biodegradable particulate organic matter, the sediment constitute a very efficient sink for nitrogen during the early period following flooding or dredging of the basin. The thickening of the sedimentary column then progressively results in an increasing release of ammonium to the water column. An equilibrium is only reached after more than 5 years in the case of the Méry basin. The time required for reaching equilibrium however strongly depends on the rate of sedimentation and the biodegradability of the organic material deposited.

A remarkable event occurring some time after flooding or dredging is an inversion of the nitrate flux across the sediment-water interface, owing to the development of an anaerobic layer, once the accumulated sedimentary column becomes deeper than the oxygen penetration layer. This was observed about 50 days after flooding in the Méry basin, but this time can vary a lot according to the input of organic material to the benthos or to the nitrate concentration in the water column.

As all these changes can deeply affect the water quality of the basin, it is often very useful to be able to predict at least their general trends. The model developed in this paper allows such predictions. It requires only the determination of a few parameters characterizing the sedimentation rate and the organic material deposited. Such a model can be used as a tool for assessing the best strategy either in the conception or the management of artificial reservoirs.

Acknowledgement

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Appendix: Derivation of the diagenetic equations

For both phytoplanktonic and detrital organic matter, the following diagenetic equation can be written:

$$\frac{\partial \, \mathrm{Corg}_i}{\partial t} = -\omega \frac{\partial \, \mathrm{Corg}_i}{\partial z} - \mathrm{ka}_i(t)\, \mathrm{Corg}_i \qquad (1)$$

ka_1, the first order degradation constant of fresh phytoplanktonic material, varies seasonally, but a stationary state is assumed to be reached instantaneously.

For the detrital material, it is considered that the profile is in equilibrium with respect to the annual mean conditions.

The solution of equation (1) can then be written:

$$\mathrm{Corg}_1 = \mathrm{C^{\circ}org}_1 \exp\left(\frac{-\mathrm{ka}_1(\mathrm{t})}{\omega} \mathrm{z}\right) \tag{2}$$

$$\mathrm{Corg}_2 = \mathrm{C^{\circ}org}_2 \exp\left(\frac{-\overline{\mathrm{ka}}_1}{\omega} \mathrm{z}\right) \tag{3}$$

in the interval $z = 0$, $z = \omega t$ where t is the time elapsed from the flooding of the basin.

The values at the sediment-water interface ($\mathrm{C^{\circ}org}_1$) are calculated from the value of the sedimentation fluxes (Forg_i):

$$\mathrm{C^{\circ}org}_1 = \mathrm{Forg}_1(\mathrm{t})/\omega \tag{4}$$

$$\mathrm{C^{\circ}org}_2 = \overline{\mathrm{Forg}_2}/\omega \tag{5}$$

where $\overline{\mathrm{Forg}_2}$ and $\overline{\mathrm{ka}}_2$ are the annual mean values of the flux of detrital organic material and its first order degradation constant.

The *vertical profile of the rate of organic matter degradation* in the sediments is then given by the following relation:

$$\text{Rate org.degr.}(\mathrm{z}, \mathrm{t}) = \mathrm{ka}_1 \mathrm{C^{\circ}org}_1 \exp\left(\frac{-\mathrm{ka}_1(\mathrm{t})}{\omega} \mathrm{z}\right) + \overline{\mathrm{ka}}_2 \mathrm{C^{\circ}org}_2 \exp\left(\frac{-\overline{\mathrm{ka}}_2}{\omega} \mathrm{z}\right) \tag{6}$$

Similarly, the rate of ammonification can be written:

$$\begin{aligned} \text{Ammonif}(\mathrm{z}, \mathrm{t}) = {} & \mathrm{ka}_1 \frac{\mathrm{C^{\circ}org}_1}{(\mathrm{C/N})_1} \exp\left(\frac{-\mathrm{ka}_1(\mathrm{t})}{\omega} \mathrm{z}\right) \\ & + \overline{\mathrm{ka}}_2 \frac{\mathrm{C^{\circ}org}_2}{(\mathrm{C/N})_2} \exp\left(\frac{-\overline{\mathrm{ka}}_2}{\omega} \mathrm{z}\right) \end{aligned} \tag{7}$$

The *depth of the aerobic layer* can be calculated from the diagenetic equation of oxygen.

$$\frac{\partial \mathrm{O}_2}{\partial \mathrm{t}} = \mathrm{Di} \frac{\partial^2 \mathrm{O}_2}{\partial \mathrm{z}^2} - \alpha \cdot \text{rate org. degr.}(\mathrm{z}, \mathrm{t}) \tag{8}$$

where α is the respiratory coefficient of the organic matter decomposed, i.e. the amount of oxygen consumed for the aerobic mineralization of a unit amount of organic carbon. Taking nitrification into account, α is about 1.3 mmoles O_2/mmoles C.

When $\omega t > z_n$, the boundary conditions of equation (8) are:

at $z = 0$, $0_2 = O_0$, oxygen concentration in the water column

$z = z_n$, $O_2 = O$ (if $zn < \omega t$)

$$\frac{\partial O_2}{\partial z} = O$$

At steady state, successive integrations of equation (8) yield:

$$\frac{\partial O_2}{\partial z} = \frac{\alpha}{Di} Forg_1(t) \exp\left(-\frac{ka_1(t)}{\omega} z\right) - \frac{\alpha}{Di} \overline{Forg_2} \exp\left(-\frac{\overline{ka_2}}{\omega} z\right) + A \tag{9}$$

and

$$O_2 = \frac{\alpha}{Di} Forg_1(t) \frac{\omega}{ka_1(t)} \exp\left(-\frac{ka_1(t)}{\omega} z\right) + \frac{\alpha}{Di} \overline{Forg_2} \frac{\omega}{\overline{ka_2}} \exp\left(-\frac{\overline{ka_2}}{\omega} z\right) + Az + B \tag{10}$$

The three boundary conditions allow determination of A, B and z_n.

$$A = \frac{\alpha}{Di} Forg_1(t) \exp\left(-\frac{ka_1(t)}{\omega} z_n\right) + \frac{\alpha}{Di} \overline{Forg_2} \exp\left(-\frac{\overline{ka_2}}{\omega} z_n\right) \tag{11}$$

$$B = O_0 - \frac{a \cdot \omega}{Di}\left(\frac{Forg_1(t)}{ka_1(t)} + \frac{\overline{Forg_2}}{\overline{ka_2}}\right) \tag{12}$$

$$\frac{\alpha}{Di} Forg_1(t) \frac{\omega}{ka_1(t)} \exp\left(-\frac{ka_1(t)}{\omega} z_n\right) + \frac{\alpha}{Di} \overline{Forg_2} - \frac{\omega}{\overline{ka_2}} \exp\left(-\frac{\overline{ka_2}}{\omega} z_n\right) + Az_n + B = 0 \tag{13}$$

Equation (13) must be solved numerically to yield the value of z_n.

This being done, the flux of oxygen across the sediment-water interface can then be written:

$$FO_2 = \alpha\left[Forg_1 \cdot \left(1 - \exp\left(-\frac{ka_1}{\omega} z_n\right)\right) + Forg_2\left(1 - \exp\left(-\frac{\overline{ka_2}}{\omega} z_n\right)\right)\right]$$

If $\omega t < zn$, then the boundary condition at $z = z_n$ is replaced by the condition:

$$z = \omega t, \frac{\partial O_2}{\partial z} = 0$$

and the flux can be written:

$$FO_2 = \alpha[Forg_1(1 - \exp(-ka_1 t)) + Forg_2(1 - \exp(-\overline{ka_2} t))] \tag{15}$$

It is then possible to write the *diagenetic equation for nitrate*, following the model of Vanderbrght and Billen (1975):

$$\frac{\partial NO_3 I}{\partial t} = Di \frac{\partial^2 NO_3}{\partial z^2} + kn \text{ for } z < z_n$$

$$\frac{\partial NO_3 II}{\partial t} = Di \frac{\partial^2 NO_3}{\partial z^2} - kd\, C_{NO_3} \text{ for } z > z_n \text{ (if } z_n \leqslant \omega t)$$

Where kn is the rate of nitrification, which, in the aerobic layer, is taken proportional to the rate of ammonification (Billen, 1982).

$$kn = kn_1 + kn_2 \frac{\gamma}{(C/N)} ka_1(t) C^\circ org_1 \exp\left(\frac{-ka_1(t)}{\omega} z\right)$$

$$+ \frac{\gamma}{(C/N)_2} \overline{ka_2}\, C^\circ org_2 \exp\left(-\frac{\overline{ka_2}}{\omega} z\right) \tag{17}$$

kd is the first order constant of denitrification which depends on the size of the denitrifying population. If it is assumed that the latter adjusts itself so that, at saturating nitrate concentration ($NO_{3_{sat}} = 100\,\mu$moles/l), denitrification would be responsible for all organic matter degradation at depth z_n, then the value of kd is given by:

$$kd = \frac{1}{NO_{3_{sat}}} \bar{\tau} \cdot \left(ka_1 C^\circ org_1 \exp\left(-\frac{ka_1}{\omega} z_n\right) + \overline{ka_2}\, C^\circ org_2 \exp\left(-\frac{\overline{ka_2}}{\omega} z_n\right)\right) \tag{18}$$

where τ is the stoechiometric coefficient relating nitrate reduction to organic carbon degradation ($\tau = 66\,\mu$moles NO_3/gC).

The boundary conditions can be written:

$$z = 0, \quad NO_3^I = NO_3^0$$

$$z = z_n, \quad NO_3^I = NO_3^{II}$$

$$\frac{dNO_3^I}{dz} = \frac{dNO_3^{II}}{dz}$$

$$z = \omega t, \frac{dNO_3^{II}}{dz} = 0$$

The steady state solution of equation (16) is the following:

for $z < z_n$:

$$NO_3^I = \frac{kn_1}{\left(\frac{ka_1}{\omega}\right)^2 \cdot Di}\left(1 - \exp\left(-\frac{ka_1}{\omega} z\right)\right) + \frac{kn_2}{\left(\frac{\overline{ka_2}}{\omega}\right)^2 \cdot Di}\left(1 - \exp\left(-\frac{\overline{ka_2}}{\omega} z\right)\right) + Az$$

$$+ NO_3^0$$

for $z > z_n$:

$$NO_3^{II} = G \exp\left(-\sqrt{\frac{kd}{Di}}(z - z_n)\right) + H \exp\left(-\sqrt{\frac{kd}{Di}}(z - z_n)\right)$$

with

$$A = \frac{1}{B}\left\{\sqrt{\frac{kd}{Di}}\left\{\frac{(H-1)}{(H+1)}\left(\sum_i \frac{\gamma\omega^2\, C^{o}org_i}{ka_i Di(C/N)_i}\left(1 - \exp\left(-\frac{ka_i}{\omega} z_n\right)\right) + NO_3^0\right\}\right\} \qquad (20)$$

$$- \sum_i \frac{\gamma\omega^2\, C^{o}org_i}{Di\cdot(C/N)_i} \exp\left(-\frac{ka_i}{\omega} z_n\right)\right\}$$

$$B = 1 + \sqrt{\frac{kd}{Di}}\frac{(1 - E)}{(1 + E)}\cdot z_n$$

$$E = \exp\left(-2\sqrt{\frac{kd}{Di}}(\omega t - z_n)\right)$$

$$G = NO_3(z_n)\frac{1}{(1 + E)}$$

$$H = NO_3(z_n)\frac{E}{(1 + E)}$$

The flux of nitrate across the sediment-water interface is then given by:

$$F_{NO_3} = -Di\left(\frac{d\,C_{NO_3}}{dz}\right)_0 = -\frac{kn_1}{\left(\frac{ka_1}{\omega}\right)} - \frac{kn_2}{\left(\frac{ka_2}{\omega}\right)} - Di\cdot A \qquad (21)$$

$$= -\gamma.\frac{Forg_1}{(C/N)_1} - \gamma\cdot\frac{Forg_2}{(C/N)_2} - Di\cdot A$$

In the case when $z_n > \omega t$, the diagenetic equation for NO_3 is simply:

$$O = \frac{\partial_{NO_3}}{\partial t} = Di\frac{\partial^2 NO_3}{\partial z^2} + kn$$

with the boundary conditions:

$$z = 0, \quad NO_3 = NO_3^0$$

$$z = \omega t, \quad \frac{d_{NO_3}}{dz} = O$$

The flux of nitrate across the sediment-water interface is then given by:

$$F_{NO_3} = -\gamma \sum_i \frac{Forg_i}{(C/N)_i} (1 - \exp(-ka_i t)) \tag{22}$$

The diagenetic equation for ammonium can be written:

$$\frac{\partial NH_4}{\partial t} = \frac{Di}{1 + K} \frac{\partial^2 NH_4}{\partial z^2} - \omega \frac{\partial NH_4}{\partial z} + \frac{1}{1 + K} R_{NH_4} \tag{23}$$

where K is the adsoprtion constant of ammonium on the solid phase of the sediment R_{NH_4} is the sum of all rates of ammonium production (ammonification) and consumption (nitrification)

$$\text{for} \quad z < z_n\,(I), \quad R_{NH_4} = (1 - \gamma \sum_i ka_i\, Norg_i^0 \exp\left(-\frac{ka_i}{\omega} z\right)$$

$$z > z_n\,(II), \quad R_{NH_4} = \sum_i ka_i\, Norg_i^0 \exp\left(\frac{ka_i}{\omega} z\right)$$

$$\text{where } Norgi^0 = \frac{C^\circ org_i}{(C/N)_i}$$

with the boundary conditions:

$$z = 0, \quad NH_4^I = NH_4^0$$

$$z = z_n, \quad NH_4^I = NH_4^{II}$$

$$\frac{dNH_4^I}{dz} = \frac{dNH_4^{II}}{dz}$$

$$z = \omega t, \quad \left(\frac{dNH_4}{dz}\right) = 0$$

The steady state solution of (23) is:

$$z < z_n\!: NH_4^I = (1 - \gamma) \sum_i \frac{\omega\, Norg_i^0}{Di\left(\frac{kd_i}{\omega} + \frac{\omega'}{Di}\right)} \exp\left(-\frac{ka_i}{\omega} z\right)$$

$$+ E + F \exp\left(\frac{\omega'}{Di} z\right)$$

$$z > z_n : NH_4^{II} = \sum_i \frac{\omega \, Norg_i^0}{Di\left(\frac{ka_i}{\omega} + \frac{\omega'}{Di}\right)} \exp\left(-\frac{ka_i}{\omega} z\right) \qquad (24)$$

$$L + M \exp\left(\frac{\omega'}{Di}(z - z_n)\right)$$

with

$$\omega' = (1 + K)\,\omega$$

$$L = C^I_{NH_4}(z_n) + \sum_i \frac{\omega \cdot Norg_i^0}{Di\left(\frac{ka_i}{\omega} + \frac{\omega'}{Di}\right)} \exp \frac{ka_i}{\omega} z_n - M$$

$$M = -\sum_i \frac{ka_i \, Norg_i^0 \exp(-ka_i t)}{\omega'\left(\frac{ka_i}{\omega} + \frac{\omega'}{Di}\right) \exp\left(\frac{\omega'}{Di}(\omega t - z_n)\right)}$$

$$N = NH_4^0 P + \sum_i \frac{\omega \, Norg_i^0 (1 - \gamma)}{Di\left(\frac{ka_i}{\omega} + \frac{\omega'}{Di}\right)}$$

$$P = \sum_i \frac{\gamma \, ka_i \, Norg_i^0}{\omega'\left(\frac{ka_i}{\omega} + \frac{\omega'}{Di}\right)} \exp\left(-\frac{\omega'}{Di} + \frac{ka_i}{\omega}\right) z_n \Big) + M \exp\left(-\frac{\omega'}{Di} z_n\right)$$

The flux of ammonium across the sediment-water interface is then given by the following relation:

$$F_{NH_4} = \frac{ka_1 \, Norg_1^0 (1 - \gamma)}{\left(\frac{ka_1}{\omega}\right) + \left(\frac{\omega'}{Di}\right)} - \frac{ka_2 \, Norg_2^0 (1 - \gamma)}{\left(\frac{ka_2}{\omega} + \frac{\omega'}{Di}\right)} - P \cdot \omega' \qquad (25)$$

In the case when $z_n > \omega t$, then the diagenetic equation for ammonium is simply:

$$O = \frac{\partial NH_4}{\partial t} = \frac{Di}{1 + K} \frac{\partial^2 NH_4}{\partial z^2} - \omega \frac{\partial NH_4}{\partial^2 z} \qquad (26)$$

$$- \frac{(1 - \gamma)}{(1 + K)} \sum_i ka_i \, Norg_i^0 \exp\left(-\frac{ka_i}{\omega} z\right)$$

with the boundary conditions:

$$z = 0, \quad NH_4 = NH_4^0$$
$$z = \omega t, \quad \frac{dNH_4}{dz} = 0$$

In this case:

$$NH_4 = -(1-\gamma)\sum_i \frac{\omega\, Norg_i^0}{Di\left(\frac{ka_i}{\omega} + \frac{\omega'}{Di}\right)} \exp\left(-\frac{ka_i}{\omega} z\right) + S + T \exp\left(\frac{\omega'}{Di} z\right) \tag{27}$$

with:

$$S = (1-\gamma)\frac{\sum_i \frac{ka_i\, Norg_i^0}{\left(\frac{ka_i}{\omega} + \frac{\omega'}{Di}\right)} \exp(-ka_i t)}{\omega' \exp\left(\frac{\omega'}{Di}\omega t\right)}$$

$$T = (1-\gamma)\sum_i \frac{\omega\, Norg_i^0}{Di\left(\frac{ka_i}{\omega} + \frac{\omega'}{Di}\right)} - S$$

and the flux across the sediment-water interface is given by:

$$F_{NH_4} = -(1-\gamma)\sum_i \frac{ka_i\, Norg_i^0}{\left(\frac{ka_i}{\omega} + \frac{\omega'}{Di}\right)} - S\omega' \tag{28}$$

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